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Structural stability of SiGe nanoparticles under "in situ" electron beam irradiation in TEM

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Abstract. The structure of amorphous and crystalline SiGe nanoparticles, embedded in a dielectric medium, SiO_2, and its stability under "in situ" electron beam irradiation is reported. High-resolution transmission electron microscopy and electron-diffraction pattern simulation by fast Fourier transform was used to analyze the crystal structure of the SiGe nanoparticles. Electron beam irradiation induces structural alternate order-disorder transitions in the nanoparticles for irradiation effects are mainly associated to the density of current. For irradiation with current densities < 7 $A \cdot cm^{-2}$ no effects are observed in the as-deposited amorphous samples, whereas in the crystallized samples, SiGe nanocrystals show higher stability and no effects are observed for irradiation densities of current < 50 $A \cdot cm^{-2}$. Irradiation with densities of current greater than these thresholds cause consecutive amorphous-crystalline or crystalline-amorphous structure transitions respectively for both amorphous and crystallized nanoparticles. A hexagonal structure is proposed for those nanocrystals obtained after irradiation in the as deposited amorphous samples.

1. Introduction

The formation of a high density of SiGe nanocrystals with uniform size, less than 5 nm, and embedded in a dielectric medium has potential applications in the fabrication of electronic and optoelectronic devices. Previous results indicate that low pressure chemical vapour deposition (LPCVD) of amorphous discontinuous SiGe films embedded in SiO_2 and their subsequent crystallization permit to obtain a homogeneous distribution of SiGe nanocrystals fully compatible with CMOS technology [1].

The crystallization process shows a strong dependence on size and for very thin layers normally higher temperatures and annealing times are required [2]. Electron and photon irradiations [3-6] have been suggested as alternative methods for crystallization, especially in isolated amorphous zones in semiconductors. TEM "in situ" electron beam irradiation can give very useful information on the crystallization mechanism in nanostructures. The electron beam can induce heating due to the energy-loss of the electrons and/or generation of defects, from either direct atoms displacement or reorganization of the dangling bonds. It is commonly accepted that the electron beam/sample interaction occurs within a column of material where heat and/or defects are generated. In this paper we study the structure modifications induced by "in situ" irradiation with a 200 kV electron beam in the electron microscope, on SiGe nanoparticles embedded in a dielectric medium, SiO_2.

2. Experimental

Multilayer structures with five periods of amorphous SiGe nanoparticles, separated by 15 nm / 40 nm thick SiO_2 interlayers and a top SiO_2 capping layer were deposited by LPCVD on (100) Si-substrates. The samples deposition was carried out according to the procedures described elsewhere [1]. The crystallization of the nanoparticles was achieved by subsequent Rapid Thermal Annealing of the samples in N_2 atmosphere at 900 ºC for times of 60 s. The average density and diameter of the nanoparticles was 2 $x10^{12}$ cm^{-2} and 4 nm respectively and remain unchanged after crystallization.

Transmission Electron Microscopy (TEM), high resolution (HREM) observation and electron beam irradiation were performed in a Philips Tecnai 20F FEG microscope operating at 200 kV, equipped with an Energy Dispersive X-Ray (EDX) analysis system. Crystallization studies were carried out by electron-diffraction simulation using Fast Fourier Transform patterns (FFT) of the HREM images. Cross-sectional specimens were prepared by mechanical grinding, dimpling and argon ion-milling of the samples with an acceleration voltage of 3 kV and an incidence angle of 8 º.

The electron current density was controlled by the condenser lens of the microscope selecting the "spot size". The current densities were measured using a Gatan US 1000 CCD and are summarized in table 1. To obtain an estimation of the energy-loss, current densities measurements have been made with and without sample for the same beam conditions. The irradiation experiments were performed with the electron beam spread on the entire CCD field of view to obtain the homogeneous irradiation of the area of interest. The interaction column diameter, or size of the electron probe, is at least three times the size of the nanostructures in order to obtain a homogeneous irradiation and to avoid displacements of the electron beam by charge effects in the SiO_2. The maximum current density and irradiation time were 70 $A{\cdot}cm^{-2}$ and 10 min, respectively. For the experimental conditions described electron irradiation of amorphous or crystalline SiGe thin films, with thickness > 25 nm, does not induces visible modifications in TEM images. Only in few cases, darkening due to surface contamination or lattice defects is observed. These current densities are low enough to permit the continuous observation and recording of live images, without introducing undesired perturbations in the samples during "in situ" irradiations.

3. Results and discussion

Electron beam irradiation of as-deposited amorphous samples with a density of current < 7 $A{\cdot}cm^{-2}$ has no visible effects on the SiGe nanoparticles. However for a current density of 44 $A{\cdot}cm^{-2}$, after an irradiation time > 0.4 min the SiGe nanoparticles suffer successive amorphous-crystalline-amorphous phase-transitions as the irradiation time proceeds. In Figure 1 two cross-sectional HREM images along the <110> direction of the Si-substrate are shown. For 7.40 min of irradiation two nanoparticles are visible one of them fully crystallized and the other one showing uncompleted crystallization; after 9 min of irradiation, only one nanocrystal is visible. Increasing the current density until its maximum value increases the average frequency for the transition between both phases from 1.5 min^{-1} for 28 $A{\cdot}cm^{-2}$ to 4 min^{-1} for 69 $A{\cdot}cm^{-2}$, but the qualitative results remain unaltered. Lattice parameter and crystal structure of the nanocrystals have been measured by FFT diffraction simulation, using the FFT pattern of the Si- substrate as an internal calibration. FFT was obtained when it was possible in undefaulted areas of the nanocrystals, an example is shown in the inset of figure 1. With the resolution achieved, the interplanar distances and angles measured are distorted from the cubic structure expected for SiGe, giving a lattice parameter of 0.59 nm, larger than that corresponding to pure Ge. The crystal structure of the nanocrystals can be better associated with a hexagonal structure of lattice parameters $a_0 = 0.62$ and $c = 0.88$ nm. The presence of defects and twinning in the nanocrystals suggest internal stress. In photon irradiated amorphous SiGe layers on thermal SiO_2 an internal stress up to 3GPa was measured associated to the crystallization process [7]. In the literature there are several examples of pressure induced hexagonal phase transition in Ge [8] and Si [5]. Unexpected hexagonal phases have been observed in nanocrystals and agglomerates, in some cases associated with a semiconductor-metal transition [8, 9]. However the difficulties of the method due to the small size of the nanocrystals, defect induced distortions and the resolution obtainable can support both crystal structures.

Spot size	Table I. Density of Current (A/cm^2)			
	Sample out	As-deposited	Sample out	Annealed sample
3	69	56	68	55
4	45	36	44	39
5	28	22	--	--
7	7	6	--	--

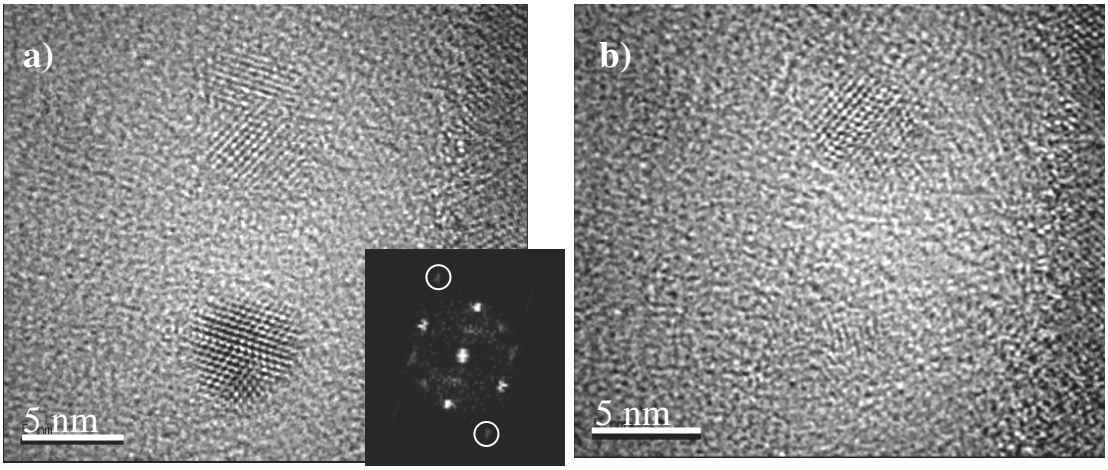

Figure1. Cross-sectional HREM image of an area irradiated with a current density of 44.1 A.cm^{-2} (a) During 7.40 min, two crystallized nanoparticles are visible. Inset: FFT pattern that can be identified as a (110) plane of a diamond structure, a_0 = 0.59 nm, or as a $(02\bar{2}1)$ plane of a hexagonal structure, a_0 = 0.62, c = 0.88 nm, low intensity spots are marked with circles. (b) Same area irradiated during 9 min, a new orientation in the only visible nanocrystal is observed.

High current density electron beam irradiations of samples crystallized at 900 ºC for 60 s induce alternate crystalline-amorphous-crystalline phase transitions. For densities of current < 50 A·cm^{-2} and irradiation times < 10 min no visible effects are observed. This current density is close to one order of magnitude larger than that needed for the first amorphous-crystalline transition in as-deposited samples (< 7 A·cm^{-2}). For a current density of 68 A·cm^{-2}, the irradiation time needed for the first phase transition is > 3 min, higher than in the as-deposited samples. The frequency of the phase transition increases as the current density does, from 1.8 min^{-1} for 44 A·cm^{-2} to 2.4 min^{-1} for 68 A·cm^{-2}. The FFT patterns show that the cubic crystal structure and the lattice parameter, a_0 = 0.55 nm, remains essentially the same during irradiation experiment, in good agreement with the nominal Ge atomic fraction, x = 0.4. Differences in stability and crystalline-amorphous transition frequency support the different crystal structure proposed for the nanocrystals formed in irradiated as-deposited samples.

The possibility that the electron beam heating and/or direct atomic displacements may drive the crystallization/amorphization process in semiconductors was extensively investigated [3-6, 10]. To study the possibility that the irradiation-induced phase changes were due to thermal annealing we have calculated the local temperature rise due to electron-irradiation [10]:

$$\Delta T = I / \pi k e(\Delta E / d) \ln(b / r_0)$$

where I is the current density, k is the thermal conductivity, e is the electron charge, $\Delta E/d$ represents the stopping power per length unit of the sample ($\cong$ 1eV/nm) and $b/r_0 = 1875$ is a geometric parameter, which describes the ratio of the diameter of the heat sink to the diameter of illuminated beam on the screen. With the maximum current density used in our experiments (I = 69 A.cm^{-2}) we have found, a maximum temperature rise $\cong$ 150ºC, well below the annealing temperature necessary for thermal crystallization.

The electron beam energy threshold for atomic displacement is 145 keV for pure Si, and 350 keV for pure Ge [11]. Since the electron energy is 200 keV, only the Si atoms bounded to other three Si atoms could be displaced. In our experiments the nanocrystals structure and lattice parameter, i.e. its composition, do not change with the irradiation current density which indicates that the main process responsible for the structural transitions is not direct atoms displacement.

During electron irradiation, a large number of collisions occur, which can produce the breaking of the dangling bonds. The energy transfer from the electrons to the sample, producing bond breaking and subsequent reorganization of the dangling bonds, leading to short range disorder, appears as the only efficient mechanism accessible to explain the observed order/disorder-disorder/order transitions.

4. Conclusions

Continuous electron beam irradiation, with an energy of 200 keV and current densities < 70 A·cm^{-2} induces sustained amorphous/crystalline phase transitions in both amorphous SiGe nanoparticles and in SiGe nanocrystals embedded in SiO_2. The irradiation time and the current density necessary for the process to start, as well as its frequency, depend on the initial structure, amorphous or crystalline, of the nanoparticles. The main difference between as-deposited amorphous and crystallized nanostructures under irradiation is the higher stability of the thermally annealed nanocrystals and the possibility of a hexagonal structure in the beam crystallized amorphous nanostructures. The mechanism of bond reorganization by the energy transferred from the electrons appears to be the most probable one.

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